Reactions of Di-μ-chloro-bis[cyclo-octa-1,5-dienerhodium(I)] with Carbon Mono-oxide and Mono-, Di-, or Tri-tertiary Phosphines, or 1,2-Bis(diphenylarsino)ethane

By **Alan R. Sanger**, Alberta Research Council, 11315-87 Avenue, Edmonton, Alberta, Canada T6G 2C2

Reactions of $[Rh_2(cod)_2Cl_2]$ (cod = cyclo-octa-1,5-diene) with CO and $PXPh_2$ (X = Et or Cl), $Ph_2P[CH_2]_nPPh_2$ (n = 1—4), 4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane (bdmo), *cis*-$Ph_2PCH{:}CHPPh_2$, $Ph_2As[CH_2]_2AsPh_2$, $(Ph_2PCH_2)_3CMe$, or $P(CH_2CH_2PPh_2)_2Ph$, give *trans*-$[Rh(CO)Cl(PXPh_2)_2]$, $[\{Rh(CO)Cl(Ph_2P[CH_2]_nPPh_2)\}_m]$ ($m = 1, n = 2$; $m = 2, n$ = 1, 3, or 4), or related complexes. Under different conditions, a complex of $Ph_2P[CH_2]_2PPh_2$ with co-ordinated diene has been obtained. An excess of $Ph_2P[CH_2]_nPPh_2$ gives $[\{Rh(Ph_2P[CH_2]_nPPh_2)_2\}Cl]$ ($n = 2$) or $[\{Rh(CO)(Ph_2P[CH_2]_nPPh_2)_2\}Cl]$ (n = 3 or 4). Reactions of these complexes of Rh^I with Cl_2, HCl, or MeI normally give the corresponding rhodium(III) complexes. Assignments of i.r. and ^{31}P n.m.r. spectral parameters have been made by internal comparisons or by comparison with the bromo-complexes, prepared by halogen-exchange reactions.

ALTHOUGH they are used frequently as catalysts, the chemistry of polyphosphine complexes of rhodium has received relatively little attention.[1] Syntheses of complexes of rhodium(I) with mono-phosphines or -arsines may be achieved by various reactions.[2-5] The diphosphine complexes $[\{Rh(CO)Cl(dppm)\}_2]$,[6,7] $[Rh(CO)Cl(dppe)]$,[6,7] $[Rh(dppe)_2]Cl$,[6-8] $[\{Rh(CO)Cl(dppen)\}_n]$,[7] $[\{Rh(dppen)_2\}\{Rh(CO)_2Cl_2\}]$,[7] and $[\{Rh(CO)(dmpe)_2\}Cl]$ [9] ($Ph_2P[CH_2]_nPPh_2$: dppm, $n = 1$; dppe, $n = 2$; dppp, $n = 3$; dppb, $n = 4$; dppen = *cis*-$Ph_2PCH{:}CHPPh_2$; dmpe = $Me_2P[CH_2]_2PMe_2$) have been described. The crystal structures of the complex $[\{Rh(Ph_2AsCH_2AsPh_2)(CO)Cl\}_2]$,[10] which is isomorphous with the diphosphine analogue, and $[\{Rh(CO)Cl(Bu^t{}_2P[CH_2]_{10}PBu^t{}_2)\}_2]$ [11] have shown that, in each case, the diphosphine (or diarsine) ligands bridge the two rhodium atoms. In contrast, the central metal atoms of the mononuclear iridium(I) or platinum(II) complexes are chelated by $Bu^t{}_2P[CH_2]_{10}PBu^t{}_2$.[11]

RESULTS AND DISCUSSION

Chloro-complexes of Rhodium(I): *Syntheses and Spectra*. —Reaction of $[Rh_2(cod)_2Cl_2]$ (cod = cyclo-octa-1,5-diene) with stoicheiometric amounts of monophosphines [equation (1)], diphosphines [equation (2)] (except dppe or dppen), triphosphines, or $Ph_2As[CH_2]_2AsPh_2$ (dpae) under an atmosphere of CO or CO and H_2 (1 : 1) gave complexes containing one carbonyl ligand per rhodium atom and no co-ordinated cod. In contrast, in the absence of CO the chlorine-bridged complex was cleaved but the product retained co-ordinated cod.[12] Reaction of dppen with $[Rh_2(cod)_2Cl_2]$ and CO gave solvated

$$[Rh_2(cod)_2Cl_2] + 4PXPh_2 \xrightarrow{CO} 2\ trans\text{-}[Rh(CO)Cl(PXPh_2)_2] + 2\ cod \quad (1)$$
$$(X = Et \text{ or } Cl)$$

$$[Rh_2(cod)_2Cl_2] + 2L \xrightarrow{CO} trans\text{-}[\{Rh(CO)ClL\}_2] + 2\ cod \quad (2)$$
$$(L = dppm, dppp, dppb, \text{ or } bdmo)$$

---

[1] W. Levason and C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, 1972, **14**, 173.

[2] J. Chatt and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 1437.

[3] D. Evans, J. Osbourn, and G. Wilkinson, *Inorg. Synth.*, 1968, **11**, 99.

[4] G. K. N. Reddy and N. M. N. Gowda, *Indian J. Chem.*, 1974, **12**, 185.

[5] P. Ugnagliati, G. Deganello, and U. Belluco, *Inorg. Chim. Acta*, 1974, **9**, 203; L. Vallarino, *J. Inorg. Nuclear Chem.*, 1958, **8**, 288.

[6] W. Hieber and R. Kummer, *Chem. Ber.*, 1967, **100**, 148.

[7] J. T. Mague and J. P. Mitchener, *Inorg. Chem.*, 1969, **8**, 119.

[8] A. Sacco and R. Ugo, *J. Chem. Soc.*, 1964, 3274.

[9] S. A. Butter and J. Chatt, *J. Chem. Soc.* (*A*), 1970, 1411.

[10] J. T. Mague, *Inorg. Chem.*, 1969, **8**, 1975.

[11] F. C. March, R. Mason, K. M. Thomas, and B. L. Shaw, *J.C.S. Chem. Comm.* 1975, 584.

[12] J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1957, 4735.

TABLE 1

Infrared and n.m.r. spectra of rhodium(I) complexes

Complex	ν(CO) [a]	δ_P [b]	^1J(Rh–P) [b]	^2J(P–P′) [b]
trans-$[Rh(CO)Cl(PEtPh_2)_2]$	1 955	85.9	122	
trans-$[Rh(CO)Cl(PPh_2Cl)_2]$	1 992	11.1	148	
$[\{Rh(CO)Cl(dppm)\}_2]$	1 968	96.8	*c*	*c*
$[\{Rh(CO)Cl(dppe)\}_2(cod)]$	2 012, 1 992	45.1 [d]	158.5	34.5
		66.7 [e]	124.5	34.5
$[Rh(CO)Cl(dppe)]$	2 010	42.2 [d]	158	34
		63.4 [e]	124	34
$[RhBr(CO)(dppe)]$	2 007	40.3 [d]	160	33
		61.6 [e]	124.5	33
$[\{Rh(CO)Cl(dppp)\}_2]$	1 958 [f]	87.1	125	
$[\{RhBr(CO)(dppp)\}_2]$	1 956	89.5	122	
$[\{Rh(CO)Cl(dppb)\}_2]$	1 957 [g]	89.1	121	
$[\{Rh(CO)Cl(bdmo)\}_2]$	1 966	87.0	124	
$[\{Rh(CO)Cl(bdpp)\}_4]$	1 964	*c*	*c*	
$[Rh(CO)Cl(tdpme)]$ *h*	2 006	102.7	98	
i	1 926			
$[\{Rh(dppen)_2\}\{Rh(CO)_2Cl_2\}]$	2 057, 1 975	44.0	133	
$[\{Rh(dpae)(CO)Cl\}_n]$	1 972			
$[\{Rh(dppe)_2\}Cl]$		55.2	133	
$[\{Rh(CO)(dppp)_2\}Cl]$	1 920	125.0 [j]	86	46
		97.3 [k]	115	46
$[\{Rh(CO)(dppb)_2\}Cl]$	1 952	Decomp. in CD_2Cl_2		
$[\{Rh(CO)_2(bdmo)_2\}Cl]$	1 974, 1 927	ABCDX [c]		

[a] Wavenumbers in cm^{-1}; KBr pellets; very strong bands. [b] Chemical shifts in p.p.m. upfield from P_4O_6; coupling constants in Hz. [c] See text. [d] *trans* to CO. [e] *trans* to Cl. [f] B_u Mode (i.r. active only); A_g mode (Raman active only), 1 984 cm^{-1}. [g] B_u Mode (i.r. active only); A_g mode (Raman active only), 1 993 cm^{-1}. [h] Four-co-ordinate Rh. [i] Five-co-ordinate Rh. [j] Axial. [k] Equatorial.

TABLE 2

Far-i.r. spectra (200—600 cm^{-1}) of $[\{RhX(CO)L\}_n]$ [a]

L =	$(PEtPh_2)_2$	dppm	dppe		dppp		dppb	dppen	dpae	(+)-bdmo	tdpme	bdpp	
X =	Cl	Cl	Cl	Br	Cl	Br	Cl	Cl	Cl	Cl	Cl	Cl	
			222vw										
		233vw		242w					234vw				
	255vw								255vw				
									274w				
		*290*vw	*289*m					*292*m	*288*m	*298* (sh)	*283*w	*298*vwb	
	*297*m	*303*vw	*298*m		*303*vw		*303*w			*307*w	*298*w		*b*
					*310*vw			*323*m	*315*m				
			333vw		334vw	322vw			338vs			344vwb	
	352w	350vw						349m				354vwb	
			366w	369vw									
			376vw	382w									
		385w	390w						398vw	396w			
							409vw	410m			407w		
	421m	420w	424w	415m	422w	430wb	427w			418w	417w	421w	*c*
		436vw		435w				437w				428w	
		458w	455w	450m	456w		460vw	455m		453m			
				462m					468vs				
	475s	482m	483m	482m		489w(sh)			478vs				
	491s	490m	489s	496s	494m		493s	490s	502w	492s	488m	491s	
	512vs	510m	516m	514s	510m	514s		517w		508vs	516s		
		522s	530s	529s	523m		520s		524m	531(sh)	529(sh)	528s	
	549w	542w	548vs	547vs	553w	548s	550w			542(sh)	540s	543m	
	580vs	570s			575s	573m	581s	566vs	569vs	571vs	568m	565w	

[a] Nujol mulls, CsI plates; L = phosphine or arsine ligands, X = Cl or Br. Wavenumbers in cm^{-1}; w = weak, m = medium, s = strong, v = very, b = broad, and sh = shoulder. [b] Italicized bands are assigned to rhodium–chlorine stretching modes. [c] Rhodium–carbonyl-stretching modes occur within this region.

$[\{Rh(dppen)_2\}\{Rh(CO)_2Cl_2\}]$.[7] With dppe the reaction product was either $[Rh(CO)Cl(dppe)]$,[6,7] or a similar product containing co-ordinated diene. The presence or absence of co-ordinated diene was inferred from elemental analyses and changes in the carbonyl region of the i.r. spectrum. No band which could be assigned to unco-ordinated alkene was observed. Strongly co-ordinated alkene could show a band at *ca.* 1 475 cm^{-1}, but this would be masked by a band (1 477 cm^{-1}) due to dppe. The nature of the reaction product apparently depended on subtle changes in the concentrations of the reagents in this case.

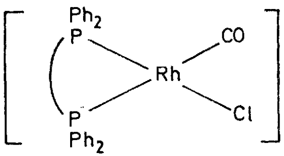
The structures of the above rhodium(I) complexes were determined from molecular-weight data, and i.r., far-i.r., and n.m.r. spectra (Tables 1 and 2).* The i.r. spectra of a number of complexes of Rh^{I}, Rh^{III}, Ir^{I}, and Ir^{III}

---

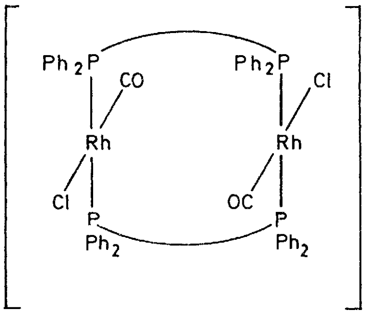
* All the ^{31}P n.m.r. spectra were recorded at −50 °C, unless otherwise stated.

[13] M. A. Bennett, R. J. H. Clark, and D. L. Milner, *Inorg. Chem.*, 1967, **6**, 1647.

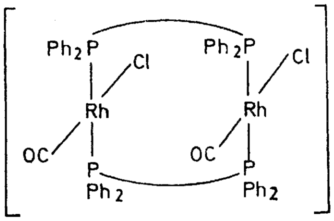
have been studied in detail.[13] The value of ν(Rh–Cl) for square-planar or octahedral complexes is within the range 250—350 cm^{-1}. The precise value depends mainly and directly on the ligand *trans* to Cl. For complexes in which the ligand *trans* to Cl is invariant the dependency of ν(Rh–Cl) on ligands *cis* to Cl is small. The complexes reported herein exhibited ν(Rh–Cl) within the range 283—323 cm^{-1}; only minor variations with a change of ligand *cis* to Cl were observed (Table 2). Assignment of bands was achieved by internal comparisons within the series, and by comparison with [RhBr(CO)(dppe)] or [{RhBr(CO)(dppp)}$_2$]. Assignments of bands close to 200 cm^{-1} as ν(Rh–Cl) for similar complexes are in error.



(1)



(2a)



(2b)

The ^{31}P n.m.r. spectra of the mononuclear complex [6,7] [Rh(CO)Cl(dppe)] (1) and the binuclear complexes of dppm, dppp, and dppb (2) have been described in a preliminary communication, [14] and the results, summarized in Table 1, are in excellent agreement with the structures shown.

The i.r. and Raman bands of the complexes of either dppp or dppb were mutually exclusive. The A_g carbonyl band (Raman active) was observed at 1 984—1 993 cm^{-1}, whereas the B_u mode (i.r. active) was observed at 1 956—1 958 cm^{-1}. For a complex of structure (2b) two carbonyl bands should be observed in both the i.r. and Raman spectra (A_1 and B_2 modes). The data confirm that structure (2a) is the structure for the complexes of dppp, dppb, or bdmo.* The ^{31}P n.m.r. spectra (—50 °C) of the diphosphine complexes each also showed a very much less intense doublet of similar parameters to the predominant doublet. These signals are assigned to the isomeric complexes (2b). The spectroscopic parameters (Table 1) of the catalytically important, optically active, complex [{Rh(CO)Cl(bdmo)}$_2$] demonstrate that this complex also adopts structure (2a).

A linear variation of [δ_P(complex) — δ_P(ligand)] with [δ_P(ligand)] has been demonstrated [15] for the complexes *trans*-[Rh(CO)Cl(PR$_3$)$_2$]. A similar linear variation was observed for all the above complexes of the mono-, di-, or tri-phosphines, using reported [16,17] values for the chemical shifts of the free ligands. The coupling constant ^1J(Rh–P) for the complex *trans*-[Rh(CO)Cl(PPh$_2$Cl)$_2$] was within the range found for *trans* complexes of the ligands PEtPh$_2$ or Ph$_2$P[CH$_2$]$_n$PPh$_2$. Because of the much greater deshielding effect of a chlorine atom bonded to phosphorus, relative to an ethyl group or polymethylene bridge, the ^{31}P chemical shift for *trans*-[Rh(CO)Cl(PPh$_2$Cl)$_2$] was considerably downfield compared to the other *trans* complexes (Table 1). A similar effect was observed for [Rh(CO)Cl$_3$(PPh$_2$Cl)$_2$] (Table 3), prepared by reaction of the above complex with chlorine (see below).

The ^{31}P n.m.r. spectrum of a solution of the products of the reaction of equimolar amounts of [Rh$_2$(cod)$_2$Cl$_2$] and (Ph$_2$PCH$_2$)$_3$CMe (tdpme) with CO did not show discrete signals for the four- and five-co-ordinate complexes of stoicheiometry Rh(CO)Cl(tdpme).[18] Instead, a doublet somewhat broader than the above spectra was observed. The coupling constant and chemical shift were intermediate between the values expected for the isomeric complexes (Table 1). These data indicate that the equilibrium reaction (3) between these isomers is rapid even at —50 °C.

The complex [{Rh(CO)Cl(bdpp)}$_n$] [bdpp = P(CH$_2$CH$_2$PPh$_2$)$_2$Ph] has been described;[19] however, the molecular weight was not reported. The complex was of low solubility in appropriate solvents, and the molecular weight herein reported is therefore less reliable than is normally desired. Also, as in the previous report,[19] consistently low carbon analyses were obtained, independent of the solvent in which the synthesis was performed. The complex appeared to be tetrameric. The carbonyl and Rh–Cl stretching modes were again characteristic of terminal CO and Cl ligands. The ^{31}P n.m.r. of a very weak but saturated solution of this complex showed a complicated set of signals, mainly doublets. The signals were of similar shifts to those of the above *trans* complexes, (2). No signals comparable to those of the complexes of dppe (1), dppen, or tdpme were observed. The

---

* bdmo = 4,5-Bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane.

[14] A. R. Sanger, *J.C.S. Chem. Comm.*, 1975, 893.

[15] B. E. Mann, C. Masters, and B. L. Shaw, *J. Chem. Soc.* (*A*), 1971, 1104.

[16] H. G. Horn and K. Sommer, *Spectrochim. Acta*, 1971, **A27**, 1049.

[17] D. L. DuBois, W. H. Myers, and D. W. Meek, *J.C.S. Dalton*, 1975, 1.

[18] W. O. Siegl, S. J. Laporte, and J. P. Collman, *Inorg. Chem.*, 1971, **10**, 2158.

[19] M. M. Taqui Khan and A. E. Martell, *Inorg. Chem.*, 1974, **13**, 2961.

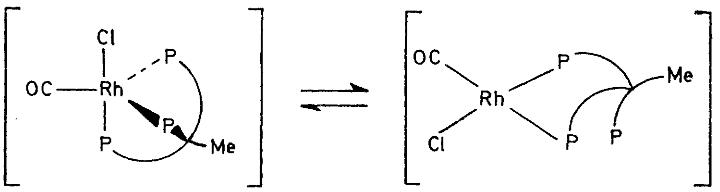
TABLE 3

Infrared and n.m.r. spectra of rhodium(III) complexes

Complex	ν(CO) [a]	ν(RhH) [b]	τ(RhH) [^1J(Rh–H)] [b]	δ_P[^1J(Rh–P)] [b]	^2J(P–H) [b]
$[Rh(CO)Cl_3(PEtPh_2)_2]$	2 107			94.5 (74)	
$[Rh(CO)Cl_3(PPh_2Cl)_2]$	2 122			31.0 (86)	
$[\{Rh(CO)Cl_3(dppm)\}_n]$	2 110			N.o.[c]	
$[\{Rh(CO)Cl_3(dppe)\}_2]$	2 094			*d*	
$[\{Rh(CO)Cl_3(dppp)\}_4]$	2 097			94.9 (96)	
$[\{Rh(CO)Cl_3(dppb)\}_3]$	2 091			N.o.	
$[\{Rh(CO)Cl_3(bdmo)\}_2]$	2 099			100.2 (73)	
$[\{RhCl_3(tdpme)\}_n]$				102.6 (105)	
$[Rh_3(dpae)_2(CO)_3Cl_8]$	2 098				
$[Rh(CO)Cl_2H(PEtPh_2)_2]$	2 050	2 101	22.3 (7.7)	92.0 (81)	5.1
$[Rh(CO)Cl_2D(PEtPh_2)_2]$	2 050	1 495 [e]			
$[\{Rh(CO)Cl_2H(dppe)\}_{1,2}]$	2 064, 1 982	2 095	N.o.	62.7 (95)	
$[\{Rh(CO)Cl_2D(dppe)\}_{1,2}]$	2 068, 1 985	1 480 [e]			
$[Rh(CO)Cl_2H(dppp)]$	2 103	2 134	23.0 (n.o.)	*ca.* 103 (br)	
$[Rh(CO)Cl_2D(dppp)]$	2 102	1 527 [e]			
$[\{Rh(CO)Cl_2H(bdmo)\}_n]$	2 073, 1 989	2 092 (sh)	*ca.* 22 (br)	*ca.* 95 (br)	
$[\{Rh(dpae)(CO)Cl_2H\}_n]$	2 005	2 095			
$[RhMe(CO)ClI(PEtPh_2)_2]$ [f]	2 071				
$[Rh(CO)(COMe)ClI(dppp)]$	2 001, 1 707 [g]				
$[\{Rh(COMe)ClI(dppp)\}]\cdot 0.5C_6H_6$	1 706 [g]				
$[Rh(CO)Cl\{Rh(COMe)ClI(tdmpe)\}_2]$	2 003, 1 703 [g]				

[a] Wavenumbers in cm^{-1}. [b] ^{31}P Chemical shifts in p.p.m. to high field of P_4O_6; coupling constants in Hz. [c] n.o. = Not observed. [d] See text. [e] ν(RhD). [f] Solution in [$^2H_6$]benzene. [g] $\nu(CH_3-CO-Rh)$.

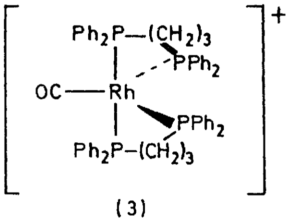
complexity of the spectrum indicated that the complex was a polymer with metal atoms cross-linking triphosphine ligands. The aggregation of the complex $[\{Rh(CO)Cl(dpae)\}_n]$ is unknown because its extremely low solubility precluded determination of its molecular weight. The i.r. and far-i.r. spectra showed that this complex also has *trans* geometry about rhodium, and has terminal CO and Cl ligands.



(3)

Reaction of a two-fold excess of the diphosphines dppp or dppb with CO and $[Rh_2(cod)_2Cl_2]$ gave $[\{Rh(CO)Cl(L)\}_2]$ and $[Rh(CO)L_2]Cl$ in equilibrium (i.r. and n.m.r.). When a five-fold excess of diphosphine was used, the latter complex predominated (i.r. and n.m.r.). Attempted isolation of the latter complex gave in each case an impure product, as evidenced by the analytical data. Nevertheless the structure of the ions $[Rh(CO)L_2]^+$ could be deduced from the ^{31}P n.m.r. spectrum (A_2B_2X) of a solution of $[Rh(CO)(dppp)_2]Cl$, contaminated with $[\{Rh(CO)Cl(dppp)\}_2]$. Two signals of similar intensity were observed at δ 125.0 [doublet of triplets, ^1J(Rh–P) 86 Hz, ^2J(P–P′) 46] and at 97.3 p.p.m. [doublet of triplets, ^1J(Rh–P) 115, ^2J(P–P′) 46 Hz]. Thus the ion was a trigonal bipyramid with an equatorial carbonyl ligand, (3). This assignment was supported by the i.r. spectrum, since the carbonyl band (1 920 cm^{-1}) was at a much lower frequency than those assigned to neutral square-planar complexes. The spectra of the dppp complex were unlike those of $[Rh(dppe)_2]Cl$ [A_4X; δ 55.2 p.p.m., ^1J(Rh–P) 133 Hz], or $[\{Rh(dppen)_2\}\{Rh(CO)_2Cl_2\}]$ [ν(CO) at 2 054 and 1 970, ν(Rh–Cl) at 292 cm^{-1}; δ 44.0 p.p.m., ^1J(Rh–P) 133 Hz]. Reaction of $[Rh_2(cod)_2Cl_2]$ with CO and a five-fold excess of dppe gave exclusively the complex [6-8] $[\{Rh(dppe)_2\}Cl]$; no carbonyl complex was observed.

Reaction of $[Rh_2(cod)_2Cl_2]$ with CO and two equivalents of bdmo in [$^2H_8$]toluene gave a solution containing complex (4; PP = bdmo). The ^{31}P n.m.r. was ‘ deceptively simple ’ [20] (ABCDX, C ~ D). The unco-ordinated PPh_2 group (P_A) was observed as a singlet (δ = 137.9 p.p.m.). The apical PPh_2 group (P_B) was observed as a doublet of triplets [δ 125.9 p.p.m.; ^1J(Rh–P) 131, $^2J(P_B-P_C)$ ~

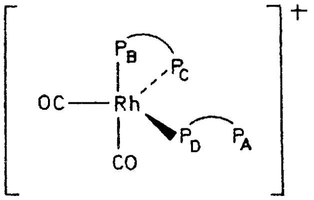


(3)

---

[20] R. J. Abraham and H. J. Bernstein, *Canad. J. Chem.*, **1961**, **39**, 216.

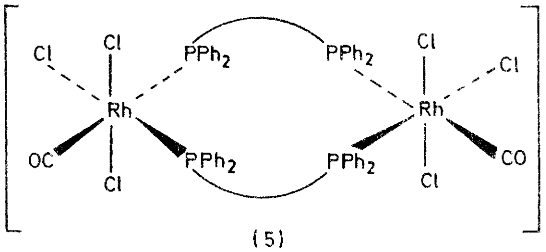
$^2J(P_B-P_D)$ 42 Hz]. The signals arising from the equatorial PPh_2 groups (P_C and P_D) were of similar shift (L→O)[20] and of very similar coupling constant to either P_B or Rh. The signals due to P_C and P_D therefore appeared as a deceptively simple doublet of doublets of doublets (δ 85.6 p.p.m.; J' 106, J'' 98, J''' 42 Hz). By comparison with the parameters for P_B, J''' is $^2J(P_B-P_C,P_D)$ and J' is $^1J(Rh-P_C,P_D)$; J'' is the separation between the observed components of the signals due to P_C and P_D. The i.r. spectrum of the complex showed two intense carbonyl bands (1 974 and 1 927 cm^{-1}). This indicates that the complex was the dicarbonyl, rather than the similar complex [Rh(CO)Cl(bdmo)$_2$] for which similar elemental analyses and ^{31}P n.m.r. spectrum would be expected.



(4)

Rhodium(III) *Complexes: Oxidative-addition Reactions of Rhodium*(I) *Complexes*.—The mono- or di-phosphine complexes of rhodium(I) in each case reacted with a dilute stream of Cl_2 in CO to give a complex of stoicheiometry [{Rh(CO)Cl$_3$(PYPh$_2$)$_2$}$_n$] (Y = Cl, Et, or polymethylene bridge). The diphosphine complexes of Rh^{III} were of relatively low solubility in appropriate solvents and there exists, therefore, a degree of uncertainty in the molecular-weight measurements reported. Nevertheless, in each case it can be stated with certainty that the products are not mononuclear. Reaction of Cl_2 in CO with [Rh(CO)Cl(tdpme)] and [{Rh(CO)Cl(bdpp)}$_4$] gave only [{RhCl$_3$(tdpme)}$_n$] and [{RhCl$_3$(bdpp}$_n$] respectively; no carbon mono-oxide complexes of Rh^{III} were detected. The reaction of chlorine with [{Rh(dpae)(CO)Cl}$_n$] gave a product or a mixture of products which could not be separated, which analysed as [{Rh$_3$(dpae)$_2$(CO)$_3$Cl$_8$}$_n$]. No band that could be assigned as ν(Rh–H) was observed in the i.r. spectrum, thus precluding structures such as [Rh$_3$(dpae)$_2$(CO)$_3$Cl$_8$H]. The material was not sufficiently soluble in appropriate solvents to permit investigation by n.m.r. or to determine the molecular weight.

The ^{31}P n.m.r. spectra (−50 °C) of the trichlororhodium(III) complexes of PEtPh$_2$, PPh$_2$Cl, dppp, dppb, or bdmo (Table 3) in each case consisted of a simple doublet [$^1J(Rh-P)$ 73—96 Hz] to high field of the corresponding complex of Rh^I. The spectra of the complex [{Rh(CO)Cl$_3$(dppe)}$_2$] at −50 and 20 °C were more complicated. Four signals of similar intensity were observed (−50 °C spectrum reported first, the 20 °C spectrum in parentheses): (*i*) doublet, 63.2, J 116 (63.2, 117); (*ii*) doublet, 60.2, 99 (59.5, 100); (*iii*) doublet of multiplets, 51.2 p.p.m., 115 Hz [50.7, 117, J' = 9], and (*iv*) doublet of multiplets, 50.8 p.p.m., 117 Hz (49.5, 119). The factors complicating these spectra are not yet understood, but may be due to the presence of complexes with inequivalent *cis*-phosphine ligands, *e.g.* (5).* The ^{31}P n.m.r. spectral parameters of [{RhCl$_3$(tdpme)}$_3$] were dissimilar from the above complexes (Table 3). All the phosphorus atoms were chemically equivalent. A *fac*-chelated complex is therefore the most probable structure for this product. During the reactions of chlorine with the above chlororhodium(I) complexes large amounts of polychlorinated hydrocarbons, mainly $C_6H_6Cl_6$, were also formed.



(5)

Reaction of solutions of mono- or di-phosphine complexes of Rh^I with a dilute stream of HCl (or DCl) in CO caused the solutions to become pale yellow or colourless. The oxidative-addition product, [{Rh(CO)Cl$_2$H(PYPh$_2$)$_2$}$_m$], was usually precipitated as a pale or white crystalline product [equation (4)]. However, the addition complexes of PEtPh$_2$, dppb, or bdmo were unstable, and consequently the pure products were not isolated in these cases. On drying *in vacuo* the white products became pale yellow. Dissolution of the precipitates into appropriate solvents (CD$_2$Cl$_2$ or CDCl$_3$) caused some dissociation and reformation of the rhodium(I) complexes (n.m.r.). Dissociation was suppressed when the product was dissolved in solvents previously saturated with HCl. The reaction of HCl with [Rh(CO)Cl(bdpp)] in refluxing methanol gave [RhCl$_3$(bdpp)].[19] Reaction of HCl with a solution of [{Rh(CO)Cl(bdmo)}$_2$] gave a solution containing an unstable complex, postulated to be [Rh(CO)Cl$_2$H(bdmo)] (Table 3), from which crystals of [{Rh(CO)Cl$_3$(bdmo)}$_2$] were slowly deposited.

$$[\{Rh(CO)Cl(PYPh_2)_2\}_n] + HCl \rightleftharpoons [\{Rh(CO)Cl_2H(PYPh_2)_2\}_m] \quad (4)$$

The ^{1}H and ^{31}P n.m.r. spectra of a solution of [Rh(CO)Cl$_2$H(PEtPh$_2$)$_2$], or the deuteriated analogue (Table 3), showed that the phosphorus nuclei were chemically equivalent, *i.e.* as in structures (6)—(8). The value of ν(CO) for the HCl adduct is very similar to that for the deuteriated complex. This implies that the carbonyl ligand is probably not *trans* to H, otherwise a resonance interaction with ν(Rh–H) would be observed.[21] The phosphine ligands are considered to be mutually *trans* in similar complexes,[13,21] and the spectral parameters of the

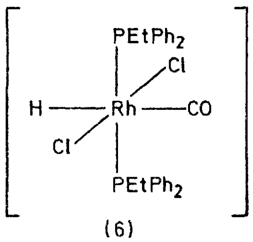
---

* The author thanks a referee for this suggestion.

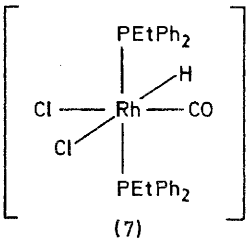
[21] H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, 1972, **72**, 231; 'Transition Metal Hydrides,' ed. E. L. Muetterties, Marcel Dekker, New York, 1971.

complex differ from those of [$Rh_2(CO)Cl_2H(dppp)$] [(8), see below]. Therefore it is deduced that [$Rh(CO)Cl_2H(PEtPh_2)_2$] adopts structure (7), corresponding to that of α-[$RhCl_2H(PR_3)_3$],[22] rather than (6) corresponding to β-[$RhCl_2H(PR_3)_3$].[22]

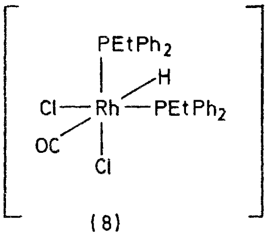
The wavenumber of the carbonyl band in the i.r. spectrum of [$Rh(CO)Cl_2H(dppp)$] is very similar to that for the deuteriated complex. This indicates that the carbonyl and hydride ligands are not mutually *trans*.[21] However, the ^1H and ^{31}P n.m.r. spectra (−50 to 10 °C) showed that the phosphorus atoms within the complex are chemically equivalent. Unless there is a rapid exchange of labile ligands at this low temperature, structure (9) is therefore precluded. The complex is monomeric, therefore its structure must be analogous to (8). The differences between the spectra of [$Rh(CO)Cl_2H(PEtPh_2)_2$] and [$Rh(CO)Cl_2H(dppp)$] support the assignment of different structures to these complexes (see Table 3).



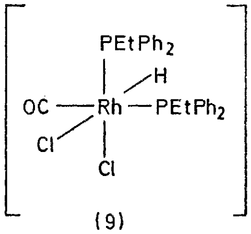
(6)



(7)



(8)



(9)

The i.r. spectra of [{$Rh(CO)Cl_2H(dppe)$}$_2$], or the deuteriated analogue, prepared in CH_2Cl_2 solution or in [$^2H_8$]toluene, each showed two terminal carbonyl-stretching bands. The ^1H n.m.r. showed only a broad resonance in the high-field region, due to Rh–*H*; no coupling to ^{103}Rh or ^{31}P could be measured. These data suggest that a dynamic equilibrium between two (or more) complexes exists in solution in this case. In contrast, the reaction of [$Rh(CO)Cl(dppe)$] with HCl in benzene gave first a colourless solution and then a white precipitate, which contained no carbonyl ligands. The reaction probably occurred in two stages [equations (5) and (6)].

$$2[Rh(CO)Cl(dppe)] + 2HCl \longrightarrow 2[Rh(CO)Cl_2H(dppe)] \quad (5)$$

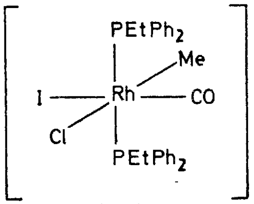
$$2[Rh(CO)Cl_2H(dppe)] \longrightarrow 2CO + [\{RhCl_2H(dppe)\}_2] \quad (6)$$

It is not clear why reaction (6) spontaneously occurred only in benzene solution, and only for the dppe complex. It is postulated that the development of a yellow colour by the above dichlorohydridorhodium(III) complexes on prolonged exposure to a vacuum is due to loss of HCl from the complex [equation (4)]. This contention has been given support by determinations of chlorine content and molecular weight in selected cases.

Addition of MeI to a stirred solution of *trans*-[$Rh(CO)Cl(PEtPh_2)_2$] under an atmosphere of CO very slowly gave a solution the spectral parameters of which indicated the presence of the oxidative-addition product, [$RhMe(CO)ClI(PEtPh_2)_2$], which probably adopts structure (10).[23] However, the material which was subsequently precipitated was contaminated with starting material and an iodine-rich complex (i.r., n.m.r., and elemental analysis). The presence of the iodine-rich material indicated that the addition reaction was reversible [equation (7); *cf.* ref. 24]. In contrast, no addition or

$$trans\text{-}[Rh(CO)Cl(PEtPh_2)_2] + MeI \rightleftharpoons [RhMe(CO)ClI(PEtPh_2)_2] \rightleftharpoons trans\text{-}[Rh(CO)I(PEtPh_2)_2] + MeCl \rightleftharpoons, etc. \quad (7)$$

exchange reaction of MeI with [{$Rh(CO)Cl(dppb)$}$_2$] was detected; the starting material was recovered unchanged. Reaction of MeI with [{$Rh(CO)Cl(dppp)$}$_2$] occurred in three stages, the second being the rapid transfer of Me from Rh to CO to form an acyl complex [equation (9)]. Subsequently CO was slowly evolved [equation (10)].



(10)

$$[\{Rh(CO)Cl(dppp)\}_2] + 2MeI \xrightleftharpoons{slow} 2\text{ ‘}RhMe(CO)ClI(dppp)\text{’} \quad (8)$$

$$\text{‘}RhMe(CO)ClI(dppp)\text{’} + 2CO \xrightleftharpoons{fast} 2[Rh(CO)(COMe)ClI(dppp)] \quad (9)$$

$$[Rh(CO)(COMe)ClI(dppp)] \xrightleftharpoons{slow} 2CO + [\{Rh(COMe)ClI(dppp)\}_2]\cdot C_6H_6 \quad (10)$$

The reactions were reversible over a period of hours. In a stream of CO the solution lost MeI by evaporation, and [{$Rh(CO)Cl(dppp)$}$_2$] was recovered.

The stereochemical requirements of two mutually *trans* bridging dppp ligands preclude structure (11). Since elimination of MeCl was disfavoured compared to elimination of MeI, I is probably *trans* to CO.[25] Since also migration of Me from Rh to CO was rapid, these ligands are mutually *cis*, and Me is probably *trans* to a

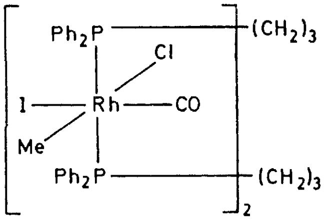
---

[22] C. E. Betts, R. N. Haszeldine, and R. V. Parish, *J.C.S. Dalton*, 1975, 2215; N. M. N. Gowda and G. K. N. Reddy, *J. Inorg. Nuclear Chem.*, 1974, **36**, 3745.

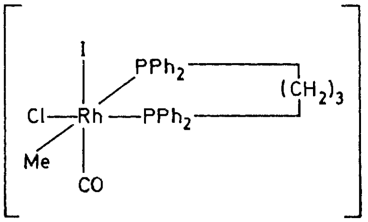
[23] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, **597**.

[24] J. E. Lyons, *J.C.S. Chem. Comm.*, 1975, 418; D. Forster, *ibid.*, p. 917.

phosphine ligand.[25] Structure (12) satisfies all the above requirements. The complexes [Rh(CO)(COMe)ClI(dppp)] and [Rh(COMe)ClI(dppp)] are monomers in solution. Therefore they also contain dppp as a chelating ligand, in octahedral and trigonal-bipyramidal complexes respectively. In each case the acyl ligand was identified by an appropriate band in the i.r. spectrum (Table 3).



(11)



(12)

EXPERIMENTAL

Except where so noted all the experiments were made in the absence of air. Benzene was dried by distillation from sodium wire in an atmosphere of dry nitrogen. The compounds $RhCl_3 \cdot 3H_2O$ and $[Rh_2(cod)_2Cl_2]$, and the phosphine and arsine ligands, were obtained commercially (Alfa Products or Strem Chemicals Inc.) and used without further treatment after satisfactory spectroscopic analyses.

Spectra were obtained using the following instruments: i.r., 0.3% in KBr pellets (Perkin-Elmer 221); far i.r. (Beckman IR11); ^1H and ^{31}P n.m.r., solutions in $[^2H_8]$-toluene or $[^2H_2]$dichloromethane (Varian HA100, with Fourier-transform capability: Digilab FTS/NMR-3 data system and pulse unit); Raman, solid state (Carson's Laboratories 10SP Ar^+–Kr^+ laser, Spex 1401 monochromator, cooled FW 130 photomultiplier, and photon-counting electronics). Analyses were by the analytical service of the Department of Chemistry, University of Alberta, Edmonton (C, H, Cl, I, and P; *M*) or by Alfred Bernhardt Mikroanalytisches Laboratorium, West Germany (C, H, As, Br, Cl, I, and P). All the i.r. and far-i.r. bands are reported in wavenumbers, ^1H n.m.r. chemical shifts (τ) are in p.p.m. ($SiMe_4$, τ 10), ^{31}P shifts (δ) are in p.p.m. to high field of P_4O_6, and coupling constants are in Hz.

Chlorination Reactions.—**CAUTION**. In all the reactions in which a solution of a chlororhodium(I) complex in benzene reacted with a dilute stream of chlorine gas in carbon mono-oxide, the reaction was exothermal and large quantities of crystalline polychlorinated aromatics, mainly $C_6H_6Cl_6$, were also produced.

Reactions of $[Rh_2(cod)_2Cl_2]$ *with Phosphines or Arsines and Carbon Mono-oxide*.—(a) *Ethyldiphenylphosphine*. (*i*) Ethyldiphenylphosphine (0.303 g, 1.415 mmol) was added dropwise to a solution of $[Rh_2(cod)_2Cl_2]$ (0.152 g, 0.617 mequiv.) in benzene (12 cm^3) under an atmosphere of CO. The solution effervesced and became pale lemon-yellow. After stirring (40 min) the solution was diluted with light petroleum (80 cm^3) to give, as pale yellow crystals, the known [2,25] complex *trans*-$[Rh(CO)Cl(PEtPh_2)_2]$ (0.313 g, 87%).

(*ii*) The known complex $[Rh(CO)Cl_3(PEtPh_2)_2]$ (0.147 g, 83%) was prepared by a published procedure.[26]

(*iii*) Reaction (3 h) of $[Rh(CO)Cl(PEtPh_2)_2]$ with HCl (or DCl) in a stream of CO gave a solution the i.r. and n.m.r. spectra of which showed only signals appropriate to $[Rh(CO)Cl_2H(PEtPh_2)_2]$ (see Table 3). However, subsequent dilution of the reaction mixture with light petroleum (5 : 1) gave, as a pale yellow precipitate, a mixture (i.r.) of starting material and $[Rh(CO)Cl_2H(PEtPh_2)_2]$. Attempts to obtain the pure oxidative-addition product were unsuccessful {Found: C, 55.8; H, 4.85; Cl, 8.95; P, 10.2. Calc. for $[Rh(CO)Cl_2H(PEtPh_2)_2]$: C, 55.15; H, 4.95; Cl, 11.25; P, 9.80%}.

(*iv*) Reaction of a benzene solution (15 cm^3) of *trans*-$[Rh(CO)Cl(PEtPh_2)_2]$ (0.438 mmol), prepared *in situ*, with excess of MeI (2.16 mmol) slowly gave a red solution. The mixture was stirred (16 h) and then diluted with light petroleum (4 : 1) to give, as a red-brown powder, a mixture of starting material and two complexes of Rh^{III} (n.m.r.). The most intense signals (>60%) in the ^{31}P n.m.r. spectrum are tentatively assigned to $[RhMe(CO)ClI(PEtPh_2)_2]$ [δ 96.0 p.p.m.; *J*(Rh–P) 93 Hz].

(b) *Chlorodiphenylphosphine*. (*i*) In a similar experiment to (a) (*i*) above, reaction of PPh_2Cl (1.86 mmol) and $[Rh_2(cod)_2Cl_2]$ (0.791 mequiv.) in benzene (25 cm^3) gave, as yellow crystals, *trans*-$[Rh(CO)Cl(PPh_2Cl)_2]$ (0.280 g, 58%) {Found: C, 49.55; H, 3.35; Cl, 17.45; P, 10.05%; *M* 658. Calc. for $[Rh(CO)Cl(PPh_2Cl)_2]$: C, 49.4; H, 3.30; Cl, 17.5; P, 10.2%; *M* 608}.

(*ii*) Reaction of the above complex with chlorine gave, as bright yellow crystals, $[Rh(CO)Cl_3(PPh_2Cl)_2]$ (53%), m.p. 152—154 °C (an orange liquid) {Found: C, 44.05; H, 3.15; Cl, 25.9; P, 9.20%; *M* 588. Calc. for $[Rh(CO)Cl_3(PPh_2Cl)_3]$: C, 44.25; H, 2.95; Cl, 26.15; P, 9.15%; *M* 679}.

(c) *Bis(diphenylphosphino)methane* (dppm). A solution of dppm (0.282 g, 0.735 mmol) in benzene (10 cm^3) was added to a solution of $[Rh_2(cod)_2Cl_2]$ (0.181 g, 0.735 mequiv.) in benzene (15 cm^3) under an atmosphere of CO. The mixture was stirred (10 min), filtered, and the precipitate was washed with light petroleum to give, as an orange powder, the known [6,7] complex $[\{Rh(CO)Cl(dppm)\}_2]$ (0.358 g, 88%).

(d) 1,2-*Bis(diphenylphosphino)ethane* (dppe). (*i*) The compound dppe (0.817 g, 2.05 mmol) was added to a solution of $[Rh_2(cod)_2Cl_2]$ (0.509 g, 2.06 mequiv.) in benzene (25 cm^3) under an atmosphere of CO and H_2 (1 : 1). The mixture was stirred (1 h) and filtered to give, as a deep yellow precipitate, $[Rh_2(cod)(CO)_2Cl_2(dppe)_2]$ (1.013 g, 80%), m.p. >108° C (decomp.) {Found: C, 60.5; H, 4.65; Cl, 6.15; P, 10.1%; *M* 500. Calc. for $[Rh_2(cod)(CO)_2Cl_2(dppe)_2]$: C, 60.15; H, 4.90; Cl, 5.75; P, 10.0%; *M* 1 238}. The product showed i.r. bands at 2 012vs and 1 992vs cm^{-1}; [Rh(CO)Cl(dppe)] showed only a band at 2 010vs cm^{-1}.[6]

(*ii*) When the above experiment was repeated at half the concentration under an atmosphere of CO and H_2 or CO

---

[25] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' Wiley, New York, 1967, p. 355.

[26] A. Sacco, R. Ugo, and A. Moles, *J. Chem. Soc.* (*A*), 1966, 1670.

alone, the product was the known[6] complex [Rh(CO)Cl(dppe)] (0.473 g, 81%).

(*iii*) When the above experiment was made using a two-fold excess of dppe the product was the known[6,7] complex $[\{Rh(dppe)_2\}Cl]$ (97%). No carbonyl complex was detected.

(*iv*) Reaction of a benzene solution of either [Rh(CO)Cl(dppe)] or the cod complex with Cl_2 in a stream of CO gave, as a pale precipitate which did not melt below 200 °C, $[\{Rh(CO)Cl_3(dppe)\}_2]$ (73%) (Found: C, 50.85; H, 4.10; Cl, 16.7; P, 9.75%; *M* 1 257. Calc. for $[\{Rh(CO)Cl_3(dppe)\}_2]$: C, 51.0; H, 3.80; Cl, 16.75; P, 9.75%; *M* 1 272}.

(*v*) Reaction of a solution of [Rh(CO)Cl(dppe)] (0.173 g, 0.307 mmol) in CH_2Cl_2 (20 cm^3) with HCl gave an orange solution. The reaction mixture was allowed to evaporate to dryness, and the orange residue was washed with light petroleum (2 h) to give, as a pale yellow powder which did not melt below 200 °C, $[\{Rh(CO)Cl_2H(dppe)\}_n]$ (n = 1 or 2) (0.056 g, 30%) {Found: C, 54.6, 53.35; H, 4.30, 4.25; Cl, 11.25; P, 10.0%; *M* 881. Calc. for $[Rh(CO)Cl_2H(dppe)]$: C, 53.95; H, 4.20; Cl, 11.8; P, 10.3%; *M* 601}. The deuteriated complex was prepared in a similar manner.

(*vi*) When the previous experiment was made in $[^2H_8]$-toluene solution a similar product was obtained as a very pale yellow precipitate. Repeating the above procedure in benzene gave, as a pale yellow precipitate which contained no carbonyl ligand (i.r.), $[\{RhCl_2H(dppe)\}_2]$ (70%) (Found: C, 53.35; H, 4.35; Cl, 12.2; P, 10.3%; *M* 1 156. Calc. for $[\{RhCl_2H(dppe)\}_2]$: C, 54.45; H, 4.40; Cl, 12.35; P, 10.8%; *M* 1 146). The complex decomposed steadily to a darker material above 110 °C. The deuteriated complex was similarly prepared.

(*vii*) Reaction of a solution of $[Rh_2(cod)_2Cl_2]$ (0.338 g, 1.38 mequiv.) in acetone (30 cm^3) sequentially with dppe (0.542 g, 1.36 mmol) and PPh_3 (0.368 g, 1.40 mmol) under an atmosphere of nitrogen slowly (7 h) gave a red solution. After 22 h a red mass had separated from the solution. The mixture was filtered to give, as an orange-brown powder, impure (n.m.r.) $[RhCl(PPh_3)(dppe)]$ (0.252 g, 23%) {Found: C, 65.95; H, 4.90; Cl, 4.05%; *M* 608. Calc. for $[RhCl(PPh_3)(dppe)]$: C, 66.15; H, 4.90; Cl, 4.45%; *M* 799}. The impurity was $[\{Rh(dppe)_2\}Cl]$ (n.m.r.). When the experiment was repeated using a seven-fold excess of PPh_3 the only products were $[\{Rh(dppe)_2\}Cl]$ and $[Rh(CO)Cl(PPh_3)_2]$,[2] identified by comparison with authentic samples.

(e) 1,3-*Bis(diphenylphosphino)propane* (dppp). (*i*) The compound dppp (0.405 g, 0.983 mmol) was added to a solution of $[Rh_2(cod)_2Cl_2]$ (0.242 g, 0.981 mequiv.) in benzene (15 cm^3) under an atmosphere of CO alone or CO and H_2 (1 : 1). The mixture was successively stirred (30 min) and filtered to give as cream crystals, *trans*-$[\{Rh(CO)Cl(dppp)\}_2]$ (0.455 g, 80%), m.p. 154—155 °C (to a red liquid) (Found: C, 57.75; H, 4.80; Cl, 6.25; P, 10.75%; *M* 903. Calc. for $[\{Rh(CO)Cl(dppp)\}_2]$: C, 58.1; H, 4.55; Cl, 6.10; P, 10.7%; *M* 1 158).

(*ii*) Reaction of $[Rh_2(cod)_2Cl_2]$ with a five-fold excess of dppp in benzene solution (3 h), and subsequent dilution of the reaction mixture with light petroleum (1 : 1), gave, as a yellow powder, a mixture of $[\{Rh(CO)(dppp)_2\}Cl]$ contaminated with the above product (n.m.r.) (>70%) (Found: C, 62.35; H, 5.05; Cl, 5.05%; *M* 985. Calc. for $[\{Rh(CO)(dppp)_2\}Cl]$: C, 66.65; H, 5.30; Cl, 3.60%; *M* 990).

(*iii*) Similarly, reaction of $[\{Rh(CO)Cl(dppp)\}_2]$ with excess of PPh_3 gave a mixture of products (i.r. and n.m.r.), including both the above complexes.

(*iv*) Reaction of chlorine with a solution of $[\{Rh(CO)Cl(dppp)\}_2]$ (0.269 g, 0.465 mequiv.) in benzene or ethanol gave, as an orange precipitate, $[\{Rh(CO)Cl_3(dppp)\}_4]$ (0.170 g, 56%), m.p. >200 °C, but darkened <200 °C (Found: C, 50.75; H, 4.15; Cl, 17.05%; *M* 2 321. Calc. for $[\{Rh(CO)Cl_3(dppp)\}_4]$: C, 51.75; H, 4.05; Cl, 16.35%; *M* 2 600).

(*v*) Similarly, reaction of HCl with a solution of $[\{Rh(CO)Cl(dppp)\}_2]$, prepared *in situ*, gave, as a white precipitate which dried to a very pale yellow powder, $[Rh(CO)Cl_2H(dppp)]$ (58%), which decomposed on melting (145—155 °C) to a red liquid {Found: C, 55.0; H, 4.40; Cl, 11.35; P, 10.15%; *M* 739. Calc. for $[Rh(CO)Cl_2H(dppp)]$: C, 54.65; H, 4.40; Cl, 11.55; P, 10.05%; *M* 615}. The deuteriated complex was similarly prepared.

(*vi*) Reaction of a benzene solution of $[\{Rh(CO)Cl(dppp)\}_2]$ (0.140 g, 0.231 mequiv.) with excess of MeI over 18 h gave an orange-yellow solution. The mixture was diluted with light petroleum (2 : 1) and filtered to give, as a brown-red powder, [Rh(CO)(COMe)ClI(dppp)] (0.030 g, 17%) {Found: C, 48.25; H, 3.80; I, 17.05%; *M* 805. Calc. for [Rh(CO)(COMe)ClI(dppp)]: C, 48.1; H, 3.90; I, 16.95%; *M* 749}.

(*vii*) When the previous experiment was repeated over a longer period (3 d) the brown precipitate was solvated [Rh(COMe)ClI(dppp)] (0.109 g, 43%) (Found: C, 50.65; H, 4.25; Cl, 4.65; I, 15.95; P, 7.85%; *M* 775. Calc. for $[\{Rh(COMe)ClI(dppp)\}]\cdot 0.5C_6H_6$: C, 50.5; H, 4.25; Cl, 4.65; I, 16.8; P, 8.15%. Calc. for [Rh(COMe)ClI(dppp)] in benzene solution: *M* 769).

(*viii*) When experiments (*vi*) or (*vii*) were repeated under a stream of CO, $[\{Rh(CO)Cl(dppp)\}_2]$ was recovered.

(f) 1,4-*Bis(diphenylphosphino)butane* (dppb). (*i*) In a similar experiment to (e) (*i*) above, the reaction of equivalent amounts of dppb and $[Rh_2(cod)_2Cl_2]$ in benzene solution gave, as cream crystals, $[\{Rh(CO)Cl(dppb)\}_2]$ (80%), m.p. >130 °C (decomp. to a dark powder) (Found: C, 58.75; H, 4.90; Cl, 5.85; P, 10.4%; *M* 1 090. Calc. for $[\{Rh(CO)Cl(dppb)\}_2]$: C, 58.75; H, 4.75; Cl, 6.00; P, 10.45%; *M* 1 186).

(*ii*) With a five-fold excess of dppb, a solution of $[Rh_2(cod)_2Cl_2]$ gave, as a very pale yellow precipitate, a mixture (i.r. and n.m.r.) of $[\{Rh(CO)(dppb)_2\}Cl]$ and the above complex (Found: C, 62.45; H, 5.15; Cl, 5.15%; *M* 1 450. Calc. for $[\{Rh(CO)(dppb)_2\}Cl]$: C, 67.15; H, 5.55; Cl, 3.50%; *M* 1 019). On dissolution in CD_2Cl_2, $[\{Rh(CO)(dppb)_2\}Cl]$ decomposed slowly, and crystals of $[\{Rh(CO)Cl(dppb)\}_2]$ were deposited.

(*iii*) Reaction of a suspension of $[\{Rh(CO)Cl(dppb)\}_2]$ (0.162 g, 0.274 mequiv.) in benzene (15 cm^3) with chlorine gave, as deep yellow crystals, $[\{Rh(CO)Cl_3(dppb)\}_3]$ (0.144 g, 80%), which decomposed without melting <200 °C (Found: C, 52.55; H, 4.30; Cl, 16.15; P, 9.10%; *M* 1 840. Calc. for $[\{Rh(CO)Cl_3(dppb)\}_3]$: C, 52.45; H, 4.25; Cl, 16.05; P, 9.35%; *M* 1 991).

(*iv*) Reaction of a solution of $[\{Rh(CO)Cl(dppb)\}_2]$ in CH_2Cl_2 with HCl in a stream of CO gave a paler yellow solution. The reaction mixture was allowed to evaporate to dryness and then the residue was washed with light petroleum to give, as a pale yellow powder, starting material contaminated with a small amount of $[\{Rh(CO)Cl_3(dppb)\}_3]$ (i.r.).

(*v*) With an excess of MeI a suspension of $[\{Rh(CO)Cl(dppb)\}_2]$ in benzene remained unchanged. The original complex (92%) was recovered.

(g) 4,5-*Bis(diphenylphosphinomethyl)*-2,2-*dimethyl*-1,3-*dioxolane* (bdmo). (*i*) Addition of (+)-bdmo (0.395 g, 0.793 mmol) to a solution of $[Rh_2(cod)_2Cl_2]$ (0.191 g, 0.777 mequiv.) in benzene (15 cm^3) gave an orange-yellow solution. The mixture was successively stirred (1 h) and slowly diluted with light petroleum (2 : 1) to give yellow crystals of [{Rh(CO)Cl[(+)-bdmo]}$_2$] (0.360 g, 70%), m.p. 158—160 °C (to a red liquid) (Found: C, 58.5; H, 4.00; Cl, 5.25; P, 9.30%; *M* 1 220. Calc. for [{Rh(CO)Cl[(+)-bdmo]}$_2$]: C, 57.8; H, 4.85; Cl, 5.35; P, 9.30%; *M* 1 330).

(*ii*) Reaction of [Rh$_2$(cod)$_2$Cl$_2$] (0.100 g, 0.406 mequiv.) with CO and two or more equivalents of bdmo in benzene (10 cm^3), or [^{2}H$_8$]toluene, gave a red solution. The mixture was allowed to evaporate to dryness under a stream of CO. The red residue was washed with light petroleum to give, as a light orange powder, [Rh(CO)$_2$(η^1-bdmo)(η^2-bdmo)]Cl (0.267 g, 58%), m.p. 142—143 °C (to a red liquid) (Found: C, 64.35; H, 5.65; Cl, 3.65; P, 9.90%; *M* 1 262. Calc. for [{Rh(CO)$_2$(bdmo)$_2$}Cl]: C, 64.5; H, 5.40; Cl, 3.00; P, 10.4%; *M* 1 191).

(*iii*) The complex [{Rh(CO)Cl(bdmo)}$_2$] (0.628 mequiv.), prepared *in situ* in benzene (15 cm^3), reacted with chlorine to give a golden-yellow solution. The mixture was diluted with light petroleum (2 : 1) to give, as golden crystals that dried to a yellow powder, [{Rh(CO)Cl$_3$[(+)-bdmo]}$_2$] (0.402 g, 91%), which did not melt $<$200 °C (Found: C, 50.05; H, 4.15%; *M* 1 445. Calc. for [{Rh(CO)Cl$_3$[(+)-bdmo]}$_2$]: C, 52.25; H, 4.40; Cl, 14.45; P, 8.40%; *M* 1 472).

(*iv*) When a solution of [{Rh(CO)Cl(bdmo)}$_2$], prepared *in situ*, was treated with HCl it became very pale. After stirring (1 h) the mixture was diluted with light petroleum (1 : 1). A precipitate which slowly developed was identified (i.r.) as the starting material contaminated with a small amount of a rhodium(III) complex.

(*v*) Repeating reaction (*iv*) in [^{2}H$_8$]toluene gave a pale yellow solution. A small portion of the solution was removed for ^{31}P n.m.r. analysis. Only a broad resonance (see Table 3) was observed. The remainder of the solution, saturated with HCl, was set aside (24 h) in a sealed container. The mixture was filtered to give, as orange-yellow crystals, impure [{Rh(CO)Cl$_3$[(+)-bdmo]}$_2$] (0.068 g, 15%), identified by comparison of i.r. and n.m.r. spectra with an authentic sample [(*iii*), above].

(*vi*) When a solution prepared by the reaction (2 d) of MeI (excess) with [{Rh(CO)Cl(bdmo)}$_2$] in benzene was diluted with light petroleum (3 : 1), the product was impure starting material.

(h) *Bis*(2-*diphenylphosphinoethyl*)*phenylphosphine* (bdpp). Under an atmosphere of CO alone or CO and H$_2$ (1 : 1), reaction of bdpp (0.428 g, 0.802 mmol) with a solution of [Rh$_2$(cod)$_2$Cl$_2$] (0.198 g, 0.803 mequiv.) in benzene (14 cm^3) gave an orange precipitate which dried to a buff powder. The carbon analysis of this product was consistently low, as observed [19] for [{Rh(CO)Cl(bdpp)}$_n$] (32—55%), m.p. $>$140 °C (decomp.) (Found: C, 57.15, 58.0; H, 4.90, 4.95; Cl, 5.35, 5.40; P, 13.2, 14.1%; *M* 2 460. [{Rh(CO)Cl(bdpp)}$_4$] requires C, 59.95; H, 4.75; Cl, 5.05; P, 13.25%; *M* 2 804). The product showed i.r. bands at 2 058w and 1 959s cm^{-1}, compared to the band (1 935 cm^{-1}) reported [19] for a product of the same stoicheiometry.

(i) 1,1,1-*Tris*(*diphenylphosphinomethyl*)*ethane* (tdpme). (*i*) Addition of tdpme (0.517 g, 0.829 mmol) to a solution of [Rh$_2$(cod)$_2$Cl$_2$] (0.215 g, 0.783 mequiv.) in benzene (25 cm^3) initially gave a yellow precipitate, which subsequently redissolved to form a red solution. After 1 h the reaction mixture was diluted with light petroleum (50 cm^3) to give, as a brick-red precipitate which dried to an orange powder, the known [18] complex [Rh(CO)Cl(tdpme)] (0.613 g, 89%), m.p. *ca.* 175 °C (decomp.).

(*ii*) When the above experiment was repeated over 18 h, the solution became yellow. Dilution of the solution with light petroleum (1 : 1) gave, as a pale yellow precipitate, [{Rh(CO)$_2$(tdpme)}Cl] contaminated (i.r.) with the above complex (0.673 g, 78%), m.p. *ca.* 180 °C (decomp. to a darker powder) (Found: C, 60.3; H, 4.90; Cl, 4.65; P, 12.1. [{Rh(CO)$_2$(tdpme)}Cl] requires C, 63.05; H, 4.80; Cl, 4.35; P, 11.35%). This complex had previously been observed, but only in solution.[18]

(*iii*) An ethanolic solution of either of the above products reacted with chlorine to give, as a pale lemon-yellow precipitate, [{RhCl$_3$(tdpme)}$_n$] (0.154 g, 66%) {Found: C, 58.6; H, 5.00; Cl, 12.7; P, 11.4%. Calc. for [RhCl$_3$(tdpme)]: C, 59.05; H, 4.70; Cl, 12.75; P, 11.15%}. The material was not sufficiently soluble in appropriate solvents to permit determination of its molecular weight.

(j) cis-1,2-*Bis*(*diphenylphosphino*)*ethylene* (dppen). To a stirred solution of [Rh$_2$(cod)$_2$Cl$_2$] (0.153 g, 0.521 mequiv.) in benzene (15 cm^3) was added dppen (0.268 g, 0.677 mmol). The mixture was stirred (1 h) and filtered to give, as bright orange-yellow crystals, [{Rh(dppen)$_2$}{Rh(CO)$_2$Cl$_2$}]·C$_6$H$_6$ (0.288 g, 75%), m.p. $>$190 °C (decomp. to a darker powder) (Found: C, 60.55; H, 4.45; Cl, 5.80; P, 10.45%; *M* 1 228. Calc. for [{Rh(dppen)$_2$}{Rh(CO)$_2$Cl$_2$}]·C$_6$H$_6$: C, 59.85; H, 4.20; Cl, 5.90; P, 10.3%; *M* 1 204). The complex retained benzene during exposure to low pressure for extended periods. but slowly lost benzene when warmed.

(k) 1,2-*Bis*(*diphenylarsino*)*ethane* (dpae). (*i*) In a similar experiment to (e)(*i*) above, dpae and [Rh$_2$(cod)$_2$Cl$_2$] reacted in benzene to give, as pale primrose-yellow crystals, [{Rh(dpae)(CO)Cl}$_n$] (0.531 g, 92%) {Found: C, 50.4; H, 3.45; As, 23.05; Cl, 5.45. Calc. for [Rh(dpae)(CO)Cl]: C, 49.7; H, 3.70; As, 22.95; Cl, 5.45%}. The complex had a very low solubility in all appropriate solvents, thus precluding determination of its molecular weight.

(*ii*) When the above experiment was repeated, but using a five-fold excess of dpae, the same complex was isolated.

(*iii*) Reaction of a suspension of the above product (0.331 g, 0.507 mequiv.) in benzene (25 cm^3) with chlorine gave an orange solution. After 80 min a deep orange precipitate had developed, which dried to an orange-yellow powder, [{Rh$_3$(dpae)$_2$(CO)$_3$Cl$_8$}$_n$] (0.291 g, 70%) {Found: C, 39.95; H, 3.05; As, 18.35; Cl, 17.4. Calc. for [Rh$_3$(dpae)$_2$(CO)$_3$Cl$_8$]: C, 40.05; H, 2.95; As, 18.15; Cl, 17.2%}. The material had insufficient solubility in appropriate solvents to permit determination of its molecular weight.

(*iv*) Reaction of a suspension of [{Rh(dpae)(CO)Cl}$_n$] in benzene with HCl gave a small amount of a pale powder, the spectral parameters of which indicated that it was [{Rh(dpae)(CO)Cl$_2$H}$_n$].

Preparation of Bromorhodium(I) *Complexes*.—(a) [RhBr(CO)(dppe)]. A mixture of [Rh(CO)Cl(dppe)] (0.383 g, 0.691 mmol) and KBr (0.4 g, excess) in acetone (40 cm^3) was heated under reflux (22 h) under CO and H$_2$ (1 : 1). The yellow solution became more orange in colour, and an orange precipitate formed. The mixture was cooled to room temperature (4 h) and the precipitate redissolved. The solution was allowed to evaporate to dryness at room temperature under a stream of CO and H$_2$. The yellow residue was washed with water (150 cm) to leave, as yellow crystals, [RhBr(CO)(dppe)] (0.310 g, 61%) {Found: C, 52.25; H, 3.90; Br, 14.0%; *M* 471. Calc. for [RhBr(CO)(dppe)]; C, 53.25; H, 3.95; Br, 13.1%; *M* 609}.

(b) [{RhBr(CO)(dppp)}$_2$]. In a similar reaction to (a), reaction of KBr and [{Rh(CO)Cl(dppp)}$_2$] in acetone gave, as buff crystals, [$\{RhBr(CO)(dppp)\}_2$] (Found: C, 53.95; H, 4.40; Br, 14.75%; *M* 1 061. Calc. for [$\{RhBr(CO)(dppp)\}_2$]: C, 53.95; H, 4.20; Br, 12.8%; *M* 1 226).

I thank Dr. T. T. Nakashima, G. Bigam, and T. Brisbane of the Department of Chemistry, University of Alberta, Edmonton, for the n.m.r. spectra, and G. Spratt and Mrs. C. Goulet for technical assistance.

[6/549 *Received, 22nd March,* 1976]